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13. ABSTRACT (Maximum 200 words) The goal of this project is to understand how variations in the molecular architecture of block and graft copolymers can be manipulated in order to develop materials with exceptional mechanical, transport, and optical properties, tailored for Army applications. We systematically explored the effect of these different molecular architectures on the nanometer scale, morphological self assembly of the materials. Our research has demonstrated, that a large number of the possible molecular variations can be represented by a single <i>molecular asymmetry parameter</i> , which we have used to develop an understanding of morphology in these materials. We have demonstrated that long range order of microphase separated morphology is reduced as the number of branch points increases in graft copolymers. Additionally, excellent elastomeric mechanical properties are obtained in graft copolymers with tetrafunctional branch points and seven or more branch points per molecule.				
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Systematic Control of Morphology and Properties Through Graft Copolymer Molecular Architecture

DAAG55-98-1-0116

FINAL REPORT

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(4) Statement of the Problem Studied

The goal of this project is to understand how variations in the molecular architecture of block and graft copolymers can be manipulated in order to develop materials with exceptional mechanical, transport, and optical properties, tailored for Army applications. The type of morphology formed as well as the relative volumes of the components and the degree of long-range order directly impact the properties of these materials in their applications as toughened elastomers, and barrier materials. As such, these materials are envisioned as components of the next generation of flexible protection for the extremities (FLEXPRO). These novel molecular architectures also have potential applications as nano-layered transparent armor and as templates for patterned electronic and optical components on smaller length scales than currently available with lithographic techniques.^{1,2}

Therefore, this project has focused first on obtaining a broad understanding of the effect of block and graft copolymer molecular architecture on morphology and long range order. Secondly, we have investigated the mechanical and transport properties of these materials in order to develop structure-property relationships for block and graft copolymers as a function of molecular architecture.

(5) Summary of Most Important Results

Gido and Mays have worked to develop synthetic methods for the production of graft copolymers of precisely controlled molecular architecture. Some of these architectures are illustrated in Figure 1 and include: mixed arm stars, and graft copolymers with either regular or random arm placement and either tetrafunctional or trifunctional branch points. We systematically explored the effect of these different molecular architectures on the nanometer scale, morphological self assembly of the materials. These results were the subject of 18 peer reviewed publications over the past four years,³⁻¹⁸ including nine publications funded by the current grant. Three more peer-reviewed publications funded by the current grant are in press. We have been able to develop a good working understanding of how branch points in the block copolymers alter morphology and control long range order.

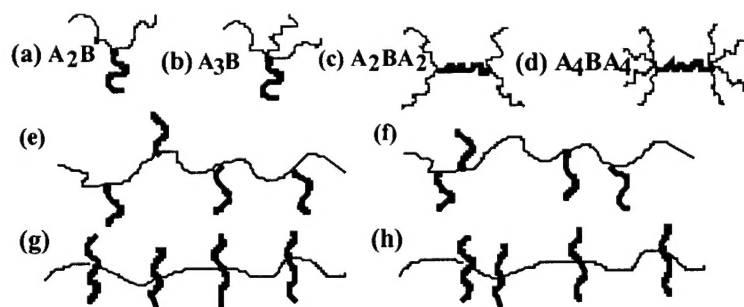


Figure 1: Branched and Grafted Block Copolymers

A goal of our research was to understand how variations in the molecular architecture of graft copolymers can be manipulated to control the nano-scale structure (morphology) and the ability to form long range order during self-assembly. In pursuit of this goal *Mays* developed new synthetic techniques to produce the precisely controlled molecular architectures, some of which are illustrated in Figure 1. *Gido* worked on relating well defined molecular architecture to morphology and properties. As a result, we have largely achieved the control of morphology and long range order of microphase separated structures through molecular design. In order to optimize performance one needs to be able to control the size, shape and symmetry, and overall volume fraction of different types of domains independently. This independent control, however, is not possible with conventional linear AB diblock copolymers and ABA triblock copolymers for which the nanophase separated morphology which forms (spheres, cylinders, cubic bicontinuous, or lamella) is tied directly to the relative volume fractions of the two block materials. For instance, if an application such as SABRE demands a material with microphase separated nanometer length scale cylinders in which the component comprising the cylindrical domain makes up over 50 volume percent of the material, linear block copolymers would not be useful.

A way to uncouple block copolymer morphology from its rigid dependence on component volume fractions is to varying molecule architecture. Our research has demonstrated, that a large number of the possible variations can be represented by a single *molecular asymmetry parameter*.^{3-5,8-11,13-16} For mixed arm star architectures such as the A₂B shown in Figure 1a, the asymmetry factor is:²⁰ $\varepsilon = (n_A/n_B)(l_A/l_B)^{1/2}$. Here (n_A/n_B) is the ratio of arm numbers of the two block types and represents the asymmetry due to the architecture. The conformational asymmetry between the two block materials is expressed by the ratio, $(l_A/l_B)^{1/2}$, where l_i is the ratio of segmental volume to the square of statistical segment length for the block material i . We have developed the methods to determine the architectural asymmetry part of a generalized asymmetry parameter for any of the various graft copolymer architectures encountered, and we have tested these methods with extensive morphological studies of model star and graft shaped block copolymers.^{3-5,8-11,13-16} We have shown that complex graft copolymer architectures with multiple grafting points (Figures 1 e through h) can be understood morphologically by analogy to fundamental building blocks defined as the average structure per junction. This fundamental component of a larger graft molecular architecture is referred to as the *constituting block copolymer*. For a graft copolymer with a backbone of A and blocks of B joined to the backbone at trifunctional branch points (Figure

1e), the constituting block copolymer is an A_2B single graft copolymer (Figure 1a) consisting of two arms of material A and one arm of material B joined at a single point.

This characterization work has also been fit into the framework of a theoretical morphology diagram calculated by S. T. Milner,²⁰ whose analysis predicts morphology as a function of composition and molecular asymmetry (architecture) for materials with a single junction point. At $\epsilon = 1$, the Milner diagram models linear, conformationally symmetric, AB diblock behavior with symmetric morphology windows around $\phi_B = 0.5$. However, as one increases the number of arms of one species relative to the other, the morphological behavior can become strongly asymmetric with respect to volume fraction. This allows us to achieve the sought after uncoupling of morphology from volume fraction: The morphology can be varied independently of volume fraction by adjusting the molecular architecture. Milner's theory is not strictly applicable to more complex, multiple graft copolymer materials. Thus, a major goal of our work has been to use the building block principle of the constituting block copolymer to understand the morphological behavior of multiple graft materials by mapping them back to the more well understood behavior of single graft materials. Experimental work has been completed and published^{3-5,8-11,13-16} which uses these ideas to develop a rational framework for predicting the morphologies of all the types of molecular architecture shown in Figure 1.

Graft Copolymers with Multiple Regularly Spaced Grafts

Within each morphological classification (spheres, cylinders, bicontinuous, and lamella) samples display a range of degrees of long range order. By long range order we are referring to the degree of perfection of the lattice symmetry, and lattice orientation, and the extent of material over which this symmetry and orientation persists. As one would expect, our work has shown that the degree of long-range order decreases with increasing molecular weight and with increasing complexity of molecular architecture.^{3,8,10,16} For applications, such as barrier or separations membranes or in optical or electronic applications, the degree of long range order may be critical in order to take full advantage of the nano-patterned structure formed by the graft copolymers. Our investigations also point toward an effect of long range order on mechanical properties. Figure 2 shows TEM images of lamellar forming graft copolymers with multiple, regularly spaced, tetrafunctional branch points (Figure 1g). The three samples from which these images were taken have the same composition, but an increasing number of grafts points per molecule. As the number of grafts increases the grain size and degree of long range order in the morphology decreases.

Balsara *et al.*^{16, 21-24} have pioneered methods based on depolarized light scattering and digital analysis of TEM micrographs which provide some measure of long range order in microphase separated block copolymer materials. These techniques yield correlation functions and correlation lengths which are representative of the length scales of the grain structures of the materials. We have collaborated with Prof. Balsara (U. California at Berkeley) in the past on determination of long-range order in block copolymers using these techniques.¹⁶ Figure 3 shows the correlation length as a function of the number of grafting junction points per molecule as measured by a number of techniques including those of Balsara. Interestingly, it is found that the decrease in grain size varies as the -2.0 power of number of grafts. We do not know the physical reason for this behavior at this time.

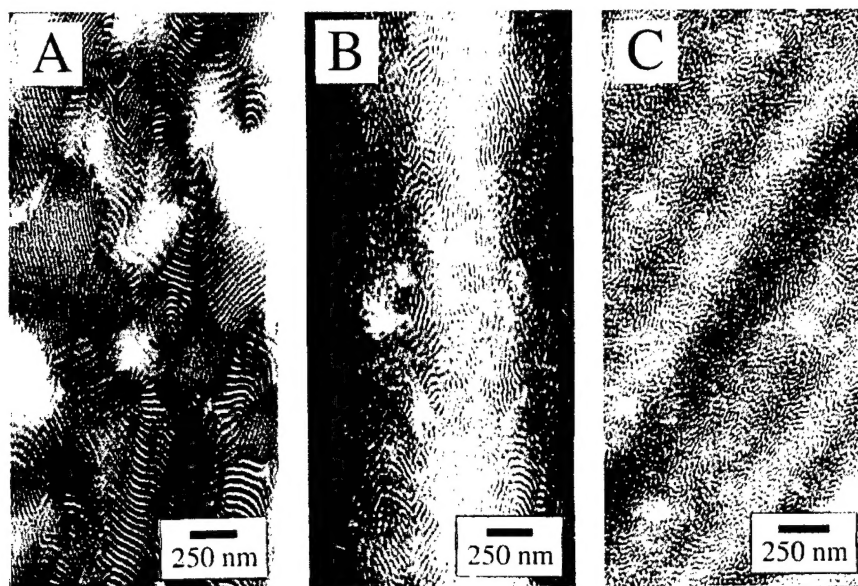


Figure 2: TEM images of lamellar structure for three samples with increasing numbers of graft points per molecule from left to right.

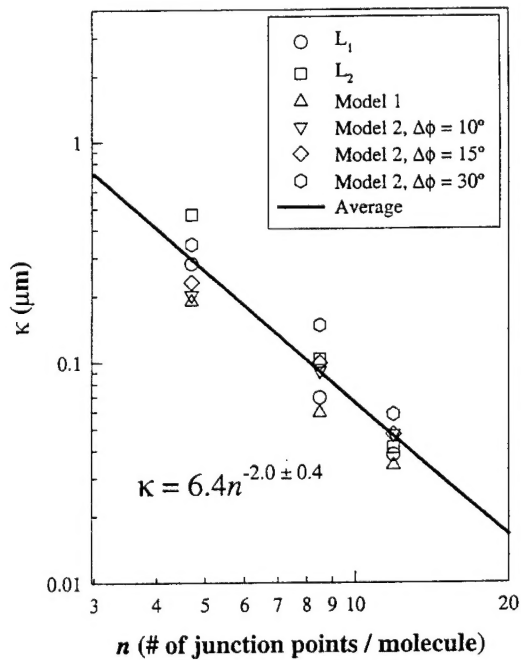


Figure 3: Correlation Length (κ) vs. number of junction points per molecule

Figure 4 shows stress vs. strain curves measured for two elastomeric graft copolymers with multiple, regularly spaced, tetrafunctional branch points (Figure 1g). These materials are thermoplastic elastomers which can be strained over 2000%. The sample with 21 volume percent polystyrene, which forms a microphase separated cylindrical morphology,¹⁶ sustains a fairly high stress of 19 MPa at the breaking point. The stress-strain behaviors of two commercial PS-PI-PS based thermoplastic elastomers sold by BASF and Shell are shown for comparison. These two materials, which are considered to have excellent mechanical properties, break at similar stresses but at much lower strains around 700% and 1000% respectively. Since the energy absorbed by a material during deformation is given by the area under the stress-strain curve, it is readily apparent that the graft copolymer elastomer has great potential in applications which require the absorption of mechanical energy, such as cushioning underlayers in flexible extremities protection. Also, this graft copolymer elastomer is clear, giving it the potential to be used in transparent armor or clear chemical-biological protective face shields.

Figure 5 shows the stress vs. strain behavior of two different tetrafunctional multigraft materials with PI backbones, PS grafts and 21 volume % PS. These materials have 5, 7 and 9 junction points per molecule respectively and they all form morphologies of PS cylinders in a PI matrix. Upon increasing the number of branch points per molecule, the long range order, as measured by grain size, decreases¹⁶ but the strength and elongation at break increases dramatically. In these materials produced by polycondensation of macromonomers the molecular weight is proportional to the number of branch points: 600,000 g/mol for 5 junctions, 840,000 g/mol for 7 junctions, and 950,000 g/mol for 9 junctions. However, the increase in strength and elongation at break in these materials with increasing number of branch points is probably not a simple molecular weight effect. The mechanical properties of PS-polydiene-PS thermoplastic elastomers based on triblock architectures are rather insensitive to molecular weight for molecular weights above about 100,000 g/mol.¹⁹ Given the relatively high molecular weights of all the regular multigraft materials, it is more likely that an architectural effect based on number of branch points underlies the dramatic increase in properties. Molecules with multiple grafting points can participate multiple reinforcing PS domains. It is also possible that decreasing long-range order, and especially decreasing grain size with increasing number of branch points also contributes to improved mechanical properties. A manuscript has recently been accepted to *Macromolecules* describing the remarkable elastomeric properties of these regular multigraft block copolymers.

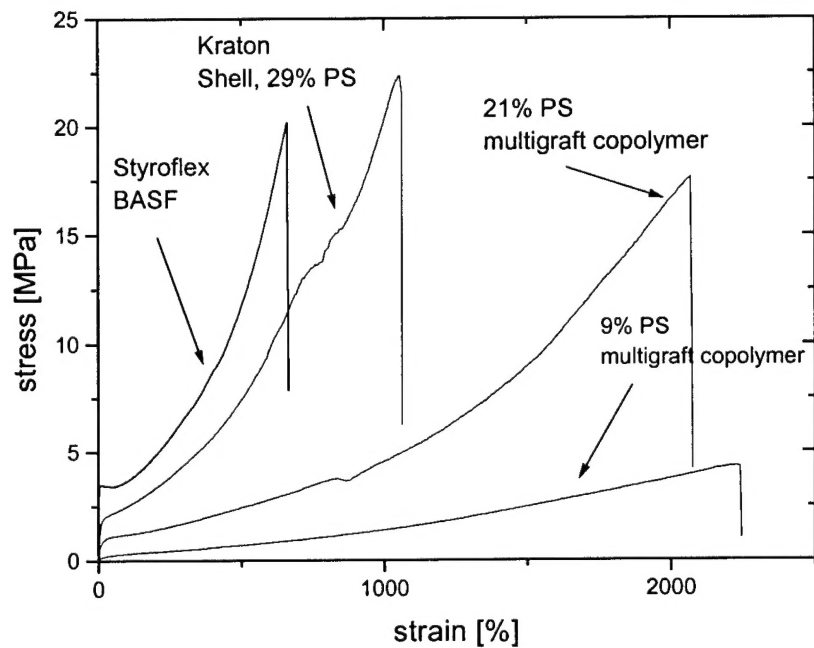


Figure 4: Stress vs. strain behavior of multigraft copolymers and two commercial thermoplastic elastomers

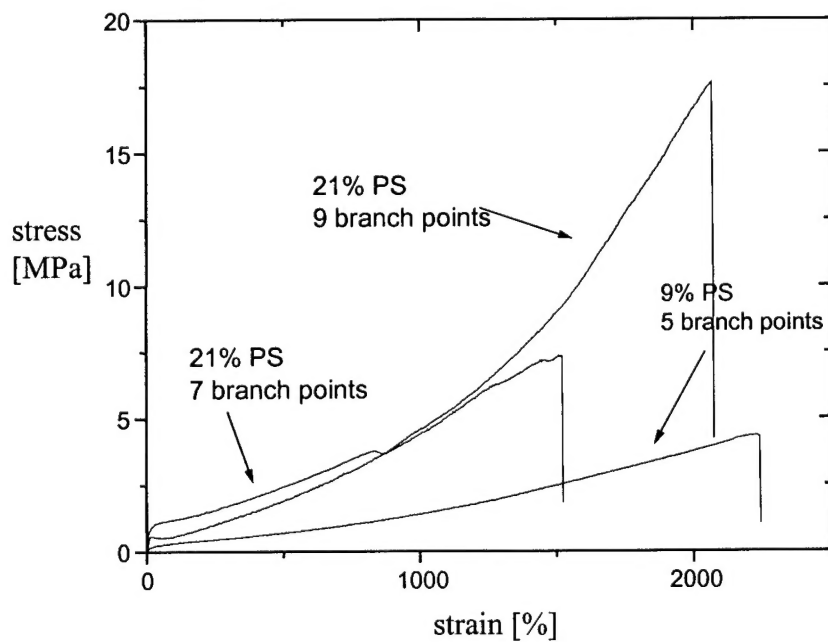


Figure 5: Stress vs. strain as a function of number of grafting points.

Transport Properties

The block and graft copolymers produced and investigated under our previous grants have contributed to the development, by Army Research Laboratory scientists of SABRE (Self Assembling Barrier Elastomer). SABRE is currently moving from fundamental research into a 6.2 development program. SABRE materials are block or graft copolymer of sulfonated polystyrene and polyisobutylene. The sulfonated polystyrene self assembles to form nanometer size hydrophilic domains with cylindrical geometries that provide pathways for water transport (and thus breathability) across the hydrophobic butyl rubber matrix. Due to their extremely small size and to their chemical functionality, these hydrophilic channels are not accessible to chemical and biological threats. Consequently we are very interested in the transport properties of microphase separated block copolymers.

We have constructed a sorption balance device that can be used to measure, diffusion coefficients, solubilities, and permeabilities of various gases and other penetrants in polymers. This device is shown in Figure 6. To date, the device has been used to make a preliminary investigation of the transport properties of several gases in block copolymers as a function of grain size, morphology, and molecular architecture. A manuscript is being prepared on these findings. Figure 7 shows how the grain size of three lamellar block copolymers was controlled by varying the casting time used to prepare sample films. Figure 8, shows that the morphologies with the smaller grain structures uniformly have higher diffusion coefficients than larger grain structure samples of the same materials. These findings are consistent with the phase continuity analysis that I am working on to explain this type of behavior.

Block Copolymer Grain Boundary Morphology

In 2000 we also did a study of a particular type of grain boundary morphology, the T-Junction, in block copolymer homopolymer blends. This work which was published in *Macromolecules* (see section 1b of this report for the reference) concluded that homopolymer segregates at the grain boundaries locally changing the morphology. This study is mainly of interest from a fundamental science point of view. However, given the importance of grain structure on transport and mechanical properties discussed above, the results may be of some practical value eventually.

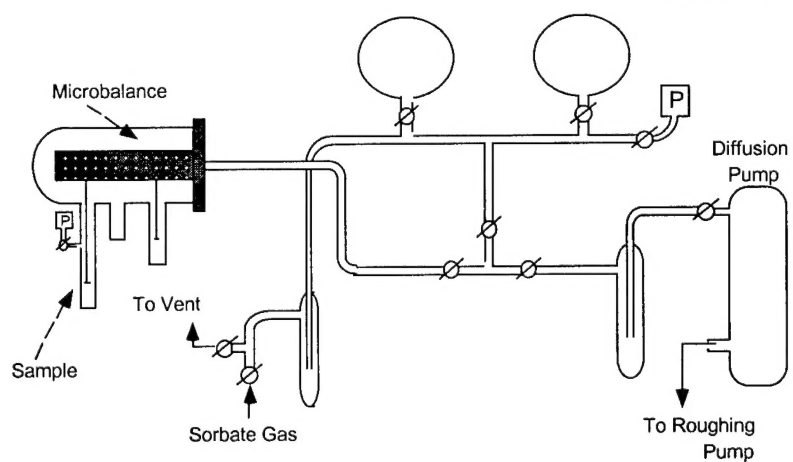
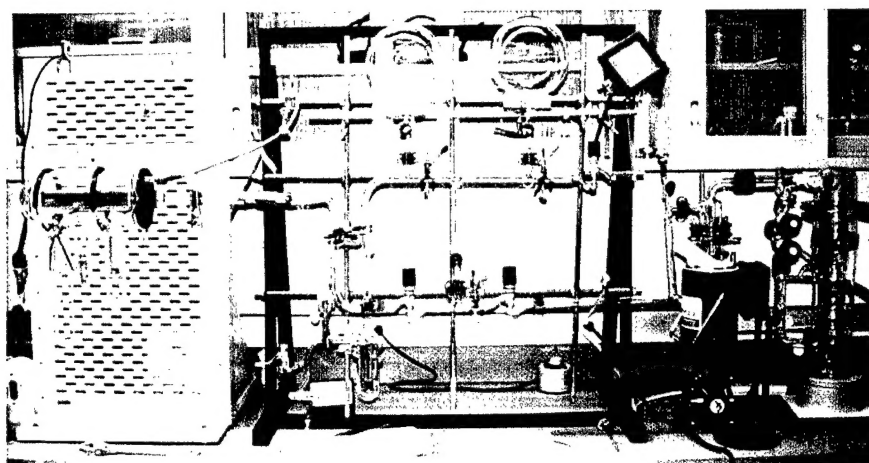
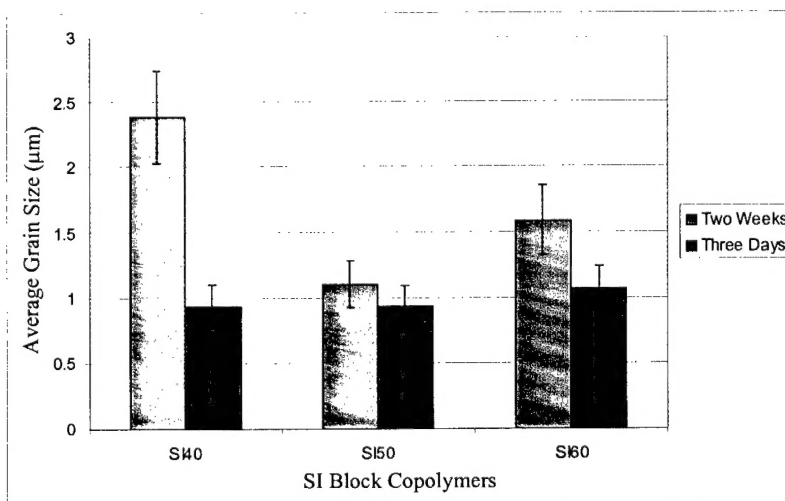


Figure 6: Sorption Balance Device for measuring transport properties of block copolymers. Photograph above and schematic below

Figure 7: Grain Size vs. casting time



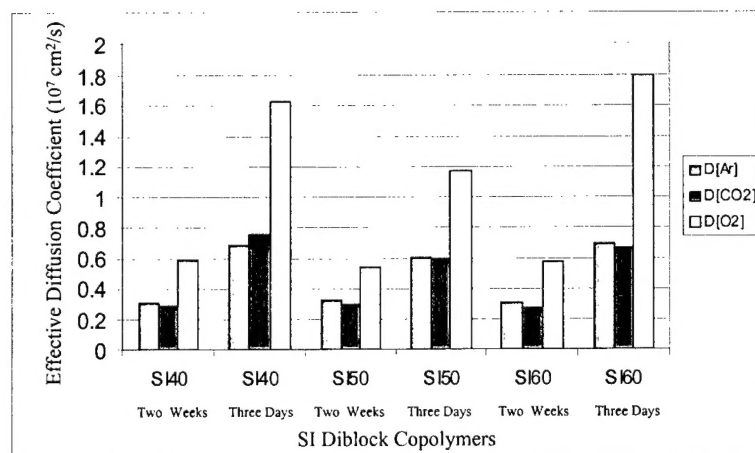


Figure 8: Diffusion Coefficient vs. Casting Time (Grain Size)

“Technology transfer” (any specific interactions or developments which would constitute technology transfer of the research results). Examples include patents, initiation of a start-up company based on research results, interactions with industry/Army R&D Laboratories or transfer of information which might impact the development of products.

Improving chemical and biological protective clothing for U. S. soldiers and industrial workers has long been an Army research priority. Standard protective clothing is made largely from butyl rubber (BR), a material whose impermeability provides an excellent level of protection but also traps heat and moisture inside the garments. BR garments are also bulky and limit dexterity; gloves constraining hand movement is a particular problem. In a desert combat environment these problems could result in more than simple discomfort and inconvenience. Microphase separated block copolymers have the potential to economically produce protective barrier materials with improved breathability, comfort and wear resistance. A strategy for doing this is to continue to exploit the excellent barrier properties of a BR matrix, while at the same time blending in block copolymers which microphase separate to form membrane spanning channels. The block copolymers of interest will therefore include polyisobutylene (PIB) blocks as well as blocks of another polymer (PS or PEO) which can be functionalized to produce the desired channel properties.

Fundamental knowledge of how to control graft copolymer morphology through molecular architecture, as well as actual materials produced under this funding, have already contributed to work by ARL scientists (Dr. Nora Beck Tan and Dawn Crawford of the Army Research Laboratory) on the development of a new class of materials for protection against chemical and biological agents while preserving breathability. These materials have elastomeric mechanical properties and are known by the acronym SABRE (Self Assembling Barrier Elastomer). SABRE is currently moving from fundamental research into a 6.2

development program. Its success illustrates our team's experience in doing fundamental research in collaboration with U.S. Army scientists which contributes to practical advances. SABRE materials are block or graft copolymer of sulfonated polystyrene and polyisobutylene. The sulfonated polystyrene self assembles to form nanometer size hydrophilic domains with cylindrical geometries that provide pathways for water transport (and thus breathability) across the hydrophobic butyl rubber matrix. Due to their extremely small size and to their chemical functionality, these hydrophilic channels are not accessible to chemical and biological threats. We have supported SABRE work at ARL by doing TEM characterization of materials produced for the program.

SABRE was developed with selective transport as the property of primary interest. Recently, we have found that when the SABRE material is based on a graft copolymer with many tetrafunctional graft points per molecule that the material has exceptional mechanical properties similar to the graft copolymers with the stress vs. strain behavior shown in Figure 4 and 5. Thus we envision SABRE materials as being useful as elastomeric energy dissipating layers as a component in new concepts for lightweight, flexible extremities protection (FLEXPRO). The fact that this layer would also simultaneously provide chemical and biological agent protection is an added advantage.

(6) List of Publications and Technical Reports

(a) Papers Published in Peer-Reviewed Journals

E. Burgaz, S. P. Gido* "T-Junction Grain Boundaries in Block Copolymer-Homopolymer Blends" *Macromolecules* **2000**, *33*, 8739.

F. L. Beyer, S. P. Gido*, C. Bueschl, H. Iatrou, D. Uhrig, J. W. Mays, M.-Y. Chang, B. Garetz, N. P. Balsara, N. Beck Tan "Graft Copolymers With Regularly Spaced Tetrafunctional Branch Points: Morphology and Grain Structure" *Macromolecules* **2000**, *33*, 2039.

F. L. Beyer, S. P. Gido*, D. Uhrig, J. W. Mays, N. Beck Tan, S. F. Trevino "Morphological Behavior of A2B2 Star Block Copolymers" *Journal of Polymer Science: Part B, Polymer Physics* **1999**, *37*, 3392.

L. Balogh*, R. Valluzzi, K. S. Laverdure, S. P. Gido, G. L. Hagnauer, and D. A. Tomalia "Formation of Silver and Gold Dendrimer Nanocomposites" *J. of Nanoparticle Research* **1999**, *3*, 1.

S. P. Gido "Asymmetry the easy way" *Nature* **1999**, *398*, 107.

J. L. David, S. P. Gido*, K. Hong, J. Zhou, J. W. Mays, and N. Beck Tan "Core-Shell Cylinder Morphology in Poly(styrene-*b*-1,3-cyclohexadiene) Diblock Copolymers" *Macromolecules* **1999**, *32*, 3216.

F. L. Beyer, S. P. Gido, G. Velis, N. Hadjichristidis, N. Beck Tan "Morphological Behavior of A₃B Miktoarm Star Block Copolymers" *Macromolecules* **1999**, 32, 6604.

C. Lee, S. P. Gido*, Y. Poulos, N. Hadjichristidis, N. Beck Tan, S. F. Trevino, and J. W. Mays " π Shaped Double Graft Copolymers: Effect of Molecular Architecture on Morphology" *Polymer* **1998**, 39, 4631.

M. Xenidou, F. L. Beyer, N. Hadjichristids, S. P. Gido*, and N. Beck Tan "Morphology of Model Graft Copolymers with Randomly Placed Trifunctional and Tetrafunctional Branch Points" *Macromolecules* **1998**, 31, 7659.

(b) Papers Published in Non-Peer Reviewed Journals or Conference Proc.

Balogh*, L., Laverdure, K. S., Gido, S. P., Mott A. G., Miller' M. J., Ketchel, B. P., Tomalia, D. A., Organic/Inorganic Hybrid Materials *Mat. Res. Soc. Symp. Proc.*, 1999, 576, 69-75.

(c) Manuscripts Submitted, but not Published

L. Yang, S. P. Gido*, J. W. Mays, S. Pispas, N. Hadjichristidis "Phase Behavior of I₂S Single Graft Block Copolymer / Homopolymer Blends" *Macromolecules* in press.

S. P. Gido "Block Copolymers: Morphological Characterization" *Encyclopedia of Materials Science and Technology*. T. P. Lodge and E. J. Kramer eds. (Elsevier: In Press)

R. Weidisch, S. P. Gido, D. Uhrig, H Iatrou, J. W. Mays, N. Hadjichristidis.
"Tetrafunctional Multigraft Copolymers as Novel Thermoplastic Elastomers"
Macromolecules in press.

(d) Technical Reports Submitted to ARO

Systematic Control of Morphology and Properties Through Graft Copolymer Molecular Architecture, Interim Progress Report 1998.

Systematic Control of Morphology and Properties Through Graft Copolymer Molecular Architecture, Interim Progress Report 1999.

Systematic Control of Morphology and Properties Through Graft Copolymer Molecular Architecture, Interim Progress Report 2000.

(7) List of Participating Scientific Personnel

Samuel P. Gido, Associate Professor.

Award: The OMNOVA Solutions Foundation, OMNOVA Solutions Signature University Award, 2000. For excellence in research and teaching.

Frederick L. Beyer, Ph.D. 1999. Currently a Researcher at the Army Research Laboratory, Aberdeen Proving Grounds, Aberdeen, MD.

Jennifer L. David, Ph.D. 1999. Supported mainly by the NSF but did about 30% of her work on ARO related projects and materials. Currently at GE Central R&D in Schenectady, NY.

Kenneth Laverdure, Graduate Student, Ph.D. expected Summer 2001, Has accepted a position at Shell.

Michael Yang, Graduate Student, Ph.D. expected Fall 2001. Has accepted at position at 3M.

Jane Zhou, Graduate Student, Ph.D. expected in 2002.

(8) Report of Inventions

None

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